Memory, Aging and Spin Glass Nature: A Study of NiO Nanoparticles

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We report studies on magnetization dynamics in NiO nanoparticles of average size 5 nm. Temperature and time dependence of dc magnetization, wait time dependence of magnetic relaxation (aging) and memory phenomena in the dc magnetization are studied with various temperature and field protocols. We observe that the system shows memory and aging in field cooled and zero field cooled magnetization measurements. These experiments show that the magnetic behavior of NiO nanoparticles is similar to spin glasses. We argue that the spin glass behavior originates from the freezing of spins at the surface of the individual particles.

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I. INTRODUCTION

The slow dynamics shown by magnetic nanoparticles has been an active area of research for the past two decades because of numerous technological applications as well as for understanding the physics behind the exotic phenomena observed.[1] Ferro and ferrimagnetic nanoparticles have been studied more than antiferromagnetic nanoparticles because of their technological potential as they have high magnetic moments.[2] Antiferromagnetic materials show a drastic change in their magnetic properties when the particle size goes to the nano regime because of the uncompensated spins at the surface which give rise to a net magnetic moment. This leads to many interesting magnetic properties e.g. a bifurcation between field cooled (FC) and zero field cooled (ZFC) magnetization, a peak in ZFC magnetization, slow relaxation of magnetization, wait time dependence of magnetization relaxation (aging) and memory in FC and ZFC magnetization measurements.[3,4,5,6,7,8,9,10,11] If the particles are non interacting, the magnetization dynamics is described by superparamagnetic relaxation as predicted by Néel-Brown theory.[12,13] On the other hand, interactions can give rise to a spin glass like behavior (superspin glass) in interacting nanoparticles.[3,5,6,7,14] However, spin glass behavior can also arise in the nanoparticles due to spin frustration at the surface of individual particles.[11,15,16,17]

Bulk Nickel oxide (NiO) is known to be antiferromagnetic with a Néel temperature T_N of 523 K. The temperature dependence of magnetization of NiO nanoparticles was first studied in 1956 by Richardson and Milligan and a peak in the magnetic susceptibility was found much below the bulk T_N.[18] It was observed that on decreasing the particle size, the magnetization increases and the peak in susceptibility shifts to lower temperatures. Later in 1961 Néel suggested that small antiferromagnetic particles should exhibit superparamagnetism and weak ferromagnetism.[19] The observed particle moment of NiO nanoparticles is found to be much larger than that predicted by the two lattice model of antiferromagnets and a multi sublattice model has been proposed to explain it and also the observed high coercivities and loop shifts in these particles.[20,21] There have been some reports on the magnetic properties of NiO nanoparticles which claim that they are superparamagnetic.[22,23,24,25,26,27] However, there are issues in considering them as superparamagnetic as their magnetization cannot be described by the modified Langevin function.[20] Tiwari et al. have done a detailed study on the magnetic properties of NiO nanoparticles and have claimed, on the basis of scaling arguments, that NiO nanoparticles show spin glass behavior.[15] They have proposed that the surface spin disorder and frustration give rise to such behavior. Winkler et al. have done magnetic measurements on both bare and polymer dispersed NiO nanoparticles of size 3 nm and have found that they can be thought to be consisting of an antiferromagnetic core with an uncompensated moment and a disordered surface shell.[16] They have proposed that the interparticle interactions can increase the effective anisotropy energy of the core magnetic moments which results in shifting the freezing temperatures to higher values and in enhancing the frustration of the spins at the surface. The behavior of NiO nanoparticles is also found to depend on the method of preparation, whether they are coated or not, and the nature of the coating.[16,22,23,28,29,30,31]

Aging and memory effects have been investigated in many nanoparticle systems using ac susceptibility and low field dc magnetization measurements with various temperature and field protocols.[5,6,7,8,10,14,32,33,34,35,36,37] Non-interacting particles are expected to show aging and memory effects only in FC magnetization measurements. These effects have been observed by various authors and their explanation is based on a simple superparamagnetic model where one assumes a distribution of anisotropy energy barriers and temperature driven dynamics.[6,8,10,37] By contrast, in interacting particles, the magnetization dynamics is spin glass like and so it is expected that they would show aging and memory effects in both FC and ZFC protocols like spin glasses. Indeed, this is the case and models based on canonical spin glasses have been used to explain these effects in such nanoparticle systems.[5,6] Thus the presence of aging and memory in ZFC protocol is like a litmus test for differentiating spin glasses and superparamagnets.

Most of the nanoparticles studied for aging and memory effects are ferro or ferrimagnetic and there are very few studies on antiferromagnetic nanoparticles. We feel that it would be interesting to study these effects in NiO nanoparticles, an antiferromagnetic system in which surface effects are known to play a major role in determining the magnetic behavior. In fact, it has been claimed that these particles show spin glass behavior.[15,16] In this work, we present a detailed study on aging and memory effects in 5 nm NiO particles with various temperature and field protocols and try to settle the issue of its spin glass nature.

II. EXPERIMENTAL DETAILS

NiO nanoparticles are prepared by the sol gel method.[15,20,26] Nickel hydroxide precursor is precipitated by reacting aqueous solutions of nickel nitrate (99.999%)and sodium hydroxide(99.99%) at pH = 12, at room temperature. This precipitate is washed many times with distilled water to remove remnant nitrate and sodium ions. It is then dried at 100°C for 6 hours to get green colored nickel hydroxide powder. Nickel oxide nanoparticles are prepared by heating nickel hydroxide at 250°C for three hours in flowing helium gas. The sample is characterized by X-ray diffraction (XRD) using a Seifert diffractometer with Cu Kα radiation. The average particle size as determined by XRD using the Scherrer formula is 5 nm. All the magnetic measurements are done with a SQUID magnetometer (Quantum Design, MPMS XL5).

III. RESULTS AND DISCUSSION

A. Aging Experiments

Temperature dependence of magnetization was done under FC and ZFC protocols at a field of 100 Oe. See Figure 1. There is a bifurcation in FC and ZFC magnetizations which manifests below 275 K and the ZFC magnetization has a broad peak at about 180 K. It can be seen that the FC magnetization increases with decreasing temperature apparently tending to saturate. Time decay of thermoremanent magnetization (TRM) was done at temperatures 25 K, 50 K and 100 K. For these measurements, we cool the sample in a field of 100 Oe to the temperature of interest and then switch off the field. Now the magnetization is measured as a function of time. See inset of Figure 1. It can be observed that the magnetization decays more or less logarithmically. This behavior is a characteristic of both superparamagnets and spin glasses. An experiment that can distinguish between the above two possibilities is the wait time dependence of magnetization relaxation (aging). We carried out aging experiments in both FC and ZFC protocols as follows: Cool the sample in a field of 100 Oe for FC (or in zero

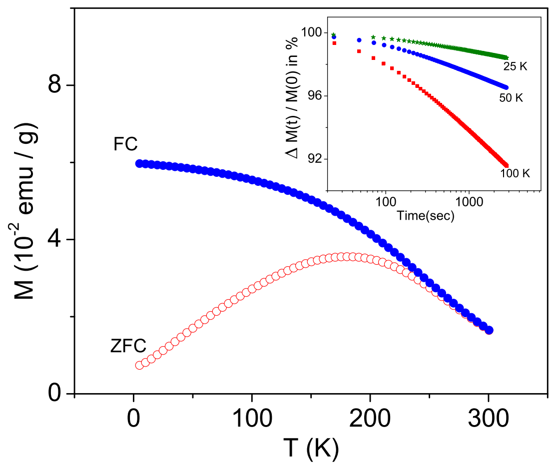

Figure 1: (Color online) Temperature dependence of the dc magnetization in a 100 Oe field for both ZFC and FC protocols. The inset shows decay of thermoremanent magnetization at temperatures 25 K, 50 K and 100 K.

field for ZFC) to the temperature of interest, wait for a specified time (wait time) and then switch the field off (or on in case of ZFC). Now record the magnetization as a function of time. Superparamagnets are expected to show a weak wait time dependence of TRM and no wait time dependence in ZFC magnetization; in other words weak FC aging and no ZFC aging. Spin glasses are, however, known to show both FC and ZFC aging.[6,38] Figure 2 shows the data for aging experiments in FC and ZFC protocols. A noticeable wait time dependence in both FC and ZFC protocols can be observed which is an evidence in support of spin glass behavior in NiO nanoparticles.

B. Memory Experiments

We carried out memory experiments in both FC and ZFC magnetization measurements. In the ZFC protocol, we first record the ZFC magnetization in the standard way and call this as the reference data. Now the sample is cooled in zero field to 5 K with a stop of one hour at 100 K. During subsequent heating the magnetization is recorded up to 300 K. In Figure 3 we show the difference in magnetization between the ZFC data with the stop and the ZFC reference data. It is clear that there is a dip at 100 K, where the stop was taken during the cooling process establishing the ZFC memory in the system. For doing FC memory experiments, the system is cooled in the presence of a magnetic field to 5 K with intermittent stops of one hour at 25 K, 50 K and 100 K with the field switched off during the stops. The magnetization is measured while cooling and then during subsequent heating. The data is shown in the inset of Figure 3. It can be observed that the system remembers the history

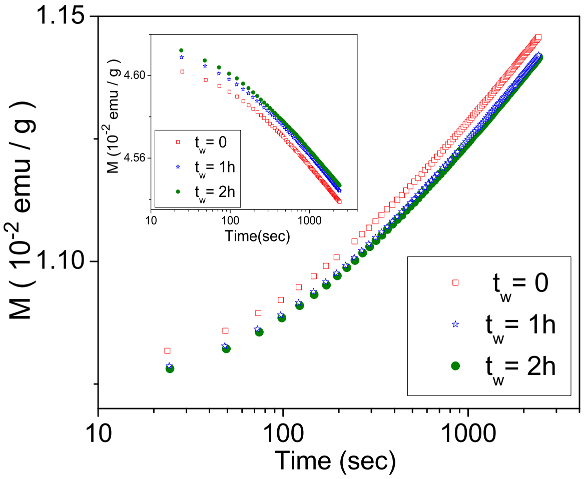

Figure 2: (Color online) Wait time dependence of ZFC magnetization at 25 K. Inset shows the wait time dependence of TRM at 25 K.

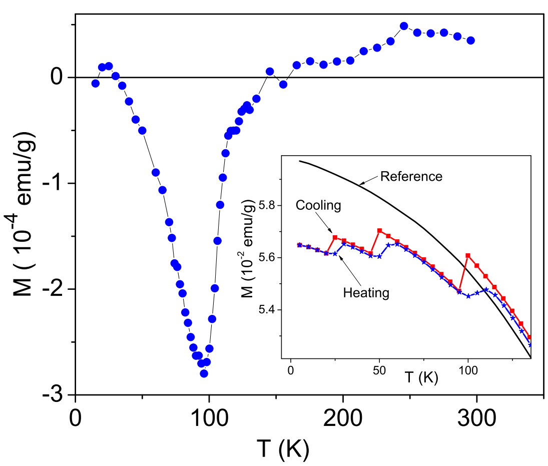

Figure 3: (Color online) Memory experiments in ZFC protocol. The difference in magnetization with a stop of one hour at 100 K in the cooling process and the reference data, plotted as a function of temperature. Inset: Memory experiments in FC protocol with stops of one hour duration at 100 K, 50 K, and 25 K. The field is switched off during each stop.

of the cooling process and the magnetization takes jumps close to the temperatures where the stops were taken.

Memory in FC magnetization has been observed for both interacting and non interacting nanoparticles and it has been shown that a broad distribution of energy barriers is sufficient to produce memory effects in FC protocol.[6] However memory in ZFC magnetization is a feature inherent to spin glasses and has not been observed in superparamagnets. Thus the memory observed in ZFC magnetization measurements provides conclusive evidence in favor of the spin glass nature of NiO nanoparticles. However, the width of the dip in Figure 3 is rather large, about 100 K, the corresponding figure for canonical spin glasses being a few Kelvins.[39]

To complement these memory experiments we have done negative temperature cycling experiments with field change in both FC and ZFC protocols as suggested by Sun et al. and adopted by many authors.[5,6,7,8,9] In FC protocol, the system is cooled to 25 K in a field of 100 Oe, the field is then switched off and the magnetization is recorded for a time period t_1. Then the system is cooled to 15 K, a field of 100 Oe is applied and magnetization data is taken for a period t_2. Temperature is now changed back to 25 K, field is switched off and magnetization is recorded again for a period t_3. Here $t_1 = t_2 = t_3$= 2800 seconds. See Figure 4(a). It can be seen that when the temperature is raised back to 25 K, the relaxation starts almost from the point at which it was left off in the previous relaxation at 25 K. Please see the inset of Figure 4(a). This shows that the system has a memory of an earlier aging in spite of an intervening aging at a lower temperature. We have also done negative temperature cycling

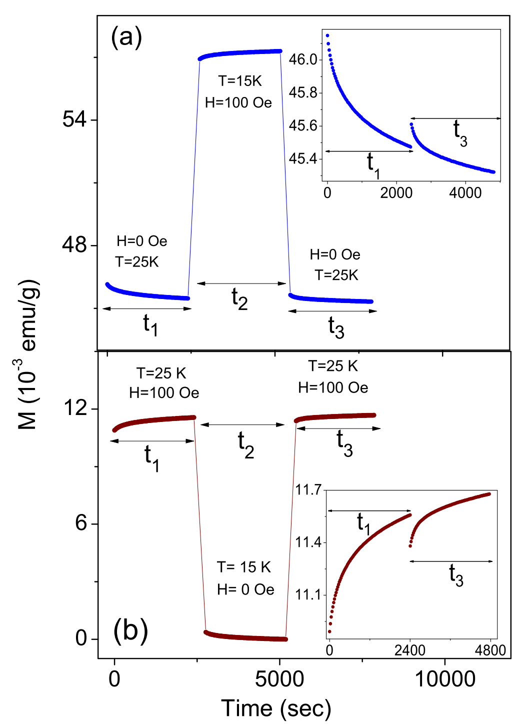

Figure 4: (Color online) Magnetic relaxation with negative temperature cycling and a field change for (a) FC protocol. (b) ZFC protocol. The insets show that the relaxation during time t_3 is essentially the continuation of the relaxation during t_1, confirming that the system has the memory of earlier relaxations.

for ZFC magnetization relaxation in a similar manner. See 4(b) and its inset. The results again confirm the existence of memory in ZFC protocol.

C. Discussion

The presence of aging and memory in ZFC magnetization of NiO nanoparticles confirms their spin glass behavior. There have been some work on other nanoparticle systems where ZFC memory was observed.[4,5,6,33,34,39] All those works were on ferri and ferromagnetic materials and the interparticle interactions were said to be responsible for the observed glassy behavior. The dip in the ZFC memory in the present work (Fig. 3) is quite broad compared to those reported on other nanoparticle systems. This suggests that the origin of spin glass behavior in NiO nanoparticles is, possibly, not interparticle interactions. In fact, the interactions between these particles are very weak and are not sufficient to cause collective freezing of particle moments at such high temperatures as has been argued by Tiwari et al.[15] However these interactions can enhance the frustration of spins at the surface of individual particles and shift the freezing temperatures to higher values.[16] The exchange bias effects observed in NiO nanoparticles indicate the presence of both ferro and antiferromagnetic interactions at the surface, which can frustrate the spins leading to spin glass behavior.[40,41] Thus the origin of spin glass state in NiO nanoparticles seems to be the freezing of spins at the surface of the individual particles. The wide dip in ZFC memory of NiO nanoparticles as compared to canonical spin glasses can possibly be attributed to the finite size of the system.

IV. CONCLUSION

We have done dc magnetic relaxation measurements on NiO nanoparticles with various temperature and field protocols. Our results show the presence of aging and memory effects in both FC and ZFC magnetizations, thus establishing the spin glass behavior of these particles. The origin of this behavior seems to be surface spin freezing of individual particles rather than interparticle interactions.

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